

THE STUDY OF HYDROGEN EVOLUTION AT p-Si  
(111) BY INTENSITY MODULATED PHOTOCURRENT  
SPECTROSCOPY AND LIGHT MODULATED MICROWAVE  
REFLECTIVITY

S. Ushiroda<sup>1</sup>, M.J. Cass<sup>2</sup>, N.W. Duffy<sup>1</sup>,  
S.R Pennock<sup>3</sup>, A.Walker<sup>2</sup>, and L.M. Peter<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, <sup>2</sup>Department of Physics,  
<sup>3</sup>Department of Electronic & Electrical Engineering,

University of Bath  
Bath BA2 7AY, GB.

The electrochemical hydrogen evolution reaction on semiconductors is a multistep process involving an adsorbed hydrogen intermediate that can in principle be desorbed either by a chemical or electrochemical route. In the case of silicon, it is not known whether the subsequent desorption of molecular hydrogen involves a second electron transfer step or the recombination of hydrogen atoms. The solution of this question will require kinetic and spectroscopic measurements to be performed at semiconductor photoelectrodes. In order to study the kinetics, frequency-resolved techniques can be used such as Intensity Modulated Photocurrent Spectroscopy (IMPS) and Light Modulated Microwave Reflectance (LMMR).

The photoinduced current for p-Si (111) in 1M fluoride solution (pH 3) is measured as a function of the potential. At more cathodic potentials photocurrent saturation is observed. IMPS and LMMR results at different potentials are shown in Fig 1 and Fig 2, respectively. It can be seen that diameters of the IMPS semicircles decrease as the potential becomes more negative. The high frequency intercept is almost constant, whereas the low frequency intercept moves away from the origin as the band bending is increased.

It is shown that the sum of the charge-transfer ( $k_{tr}$ ) and recombination rate constants ( $k_{rc}$ ) found from the IMPS measurements is the same as that derived by LMMR. This confirms that the microwave measurements provide access to the total rate constant for the consumption of surface charge by recombination and interfacial charge-transfer, even in the potential region where IMPS measurement can no longer be used.

Time resolved photocurrent measurements in the saturation region do not give useful information. However, the time dependence of the microwave response illustrated in Fig 3 shows clearly the build-up and decay of electrons at the interface.

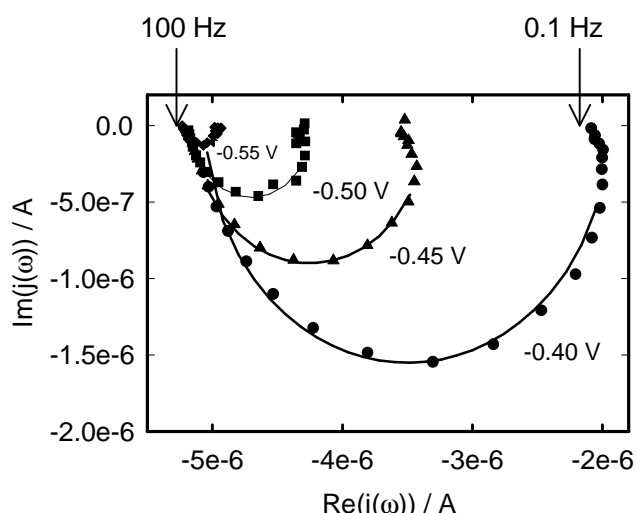


Figure 1: IMPS plots at different potentials.

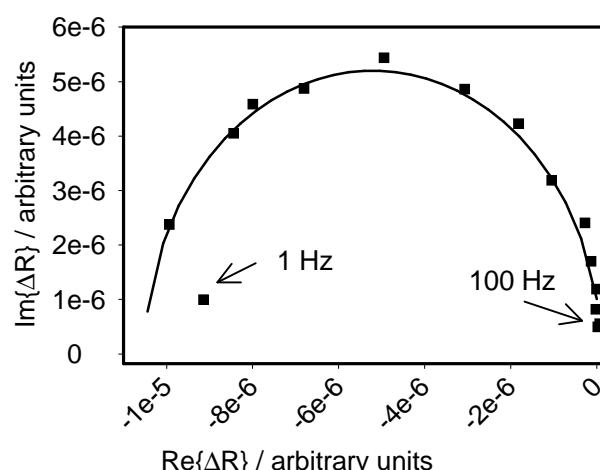


Figure 2: LMMR plot at  $-0.55$  V.

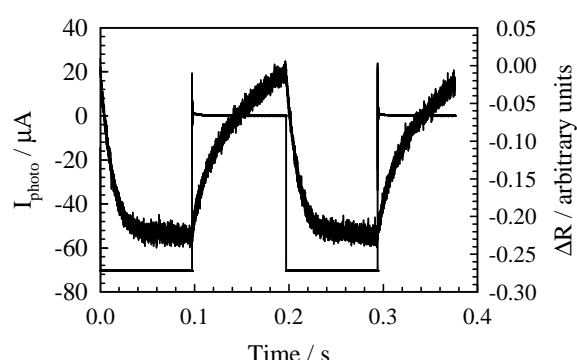


Figure 3: Time-dependent microwave response at  $-0.7$  V.

# References

1. G.Schlichthorl, E.A.Ponomarev, and L.M.Peter, *J.Electrochem.Soc.*, **142**, 3062, (1995).
2. L.M. Peter, 'Comprehensive chemical kinetics, vol.37, p 223', Elsevier, 1999.
3. L.M. Peter and D. Vanmaekelbergh, 'Advances in electrochemical science and engineering, vol.6, p 77', Wiley-Vch, 1999.